

Computational Analysis of Combustion of Separated Coal-Gas in O₂/CO₂

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Abstract

This paper analyzes oxycombustion in novel power systems that separate gasified coal into hydrogen and carbon-rich fuels. The carbon-rich fuel burns in a stoichiometric mixture of oxygen and recycled carbon dioxide (O₂/CO₂), providing a CO₂-rich product stream for sequestration. For CO₂ recycle levels between 5% and 15%, the minimum (blowout-limited) combustor residence time is calculated using a perfectly stirred reactor model with detailed chemical kinetics from the GRIMech model. Combustion occurs at conditions based on the GE H series gas turbine: pressure of 23 bars, and adiabatic flame temperature of 1800 K. Four fuel compositions are considered, corresponding to separation by metallic and polymer membranes and gasification with the Texaco and Shell processes. Results are compared to those of a methane/air system burning under the lean conditions typical of stationary power generation. The stability of the novel power systems' combustion is comparable to that of the natural-gas/air system, as indicated by similar heat release throughputs at extinction.

Introduction

Concerns over greenhouse gas emissions have sparked many ideas on the removal of CO₂ from stationary power generation systems and its long-term sequestration. Although tested technologies can remove CO₂ from the exhaust of existing power plants, more promising options involve novel power plant designs that make CO₂ removal simpler and more energy-efficient (Bolland and Saether, 1992; Singh et al., 2001). One such option is the oxycombustion power plant. In this scheme, fuel is burned in oxygen mixed with recycled combustion products or recycled CO₂, yielding a CO₂-rich exhaust stream that is readily prepared for sequestration. This scheme has been of particular interest as a way of using the carbon-rich (hydrogen-depleted) portion of coal gases, from which hydrogen has been separated for mobile applications (Hendriks, 1994).

The present study focuses on the combustor in an oxycombustion gas turbine power plant. Although exit temperature and operating pressure will probably be similar to those in non-sequestering power plant combustors, differences in the fuel, oxidant and diluent concentrations may have substantial effects on the chemical reaction rates encountered and consequently required combustor size for a given power output. We perform extinction calculations with a simple perfectly-stirred reactor (PSR) model to predict the effect of operating conditions on maximum throughput per combustor volume. Specifically, we examine the effects of fuel composition and dilution level, and make comparisons to conditions for non-sequestering power plants. Oxycombustion inlet conditions giving substantially smaller throughputs at extinction than non-sequestering plants imply that new and perhaps challenging combustor designs will be required. This information is useful in optimizing overall plant design, providing input on questions such as how much CO₂ should be recycled, and how much H₂ can be removed from the fuel stream without compromising combustor operation.

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Approach: Combustion Modeling

Gas turbine combustors can be either premixed or non-premixed and are characterized by vigorous turbulent mixing. Key design concerns are stability (blowout, flashback, and turndown ratio, and loading capacity), emissions, and exit temperature uniformity. Current stationary combustors generally use lean premixed combustion, which yields low NO_x emissions at the cost of narrower stability limits (Brewster et al., 1999). For CO₂-sequestering power plants, exit temperature and stability concerns remain, but emissions are probably a much smaller concern as pollutants may be sequestered along with the CO₂, or removed from the exhaust relatively simply.

Creating predictive models of gas turbine combustors, with realistic geometries, chemical kinetics, and turbulent flows, is an active research area (Brewster et al., 1999). However, a much simpler approach has yielded many insights into combustor operation: Gas turbine combustor behavior can be approximated in a laboratory-scale well-mixed (usually jet-stirred) reactor (Sturgess and Shouse 1997, Zelina and Ballal, 1995), and this type of well-stirred reactor can be modeled as a perfectly stirred reactor or series of perfectly stirred and/or plug flow reactors. This type of computational model has been used to predict lean blowout limits (Sturgess et al., 1991) and NO_x emissions (Bengtsson et al., 1998, and Rutar et al., 2002) for laboratory scale jet-stirred reactors. Our approach in the current work is to calculate extinction conditions for a single perfectly stirred reactor (PSR) with the same inlet properties as the combustor of interest. Though the extinction throughputs predicted with this simple model will not agree with practical combustor blowout conditions, the calculations will allow a comparison between different sets of operating conditions.

The PSR model treats the contents of the combustor as a spatially uniform mixture of gases, with inlet properties specified and exit properties equal to properties inside the reactor. The reactor is treated as adiabatic and steady state. Kinetic and thermochemical data are specified for all reactions and species present, using the GRI-Mech 2.11 database (Bowman et al., 1995), with nitrogen chemistry removed. Wall reactions are neglected, and thus extinction conditions can be expressed in terms of a single parameter: residence time in the reactor. No details of flow or geometry need be supplied; instantaneous perfect mixing of the reactant stream into the reactor contents is assumed.

PSR extinction calculations were implemented with an arc-length continuation program (Ren and Pope, 2004) making use of Chemkin subroutines (Kee et al., 1980). In this program, PSR exit conditions are calculated for a variety of different residence times, τ : The inverse of the residence time, $1/\tau$, is gradually decreased until extinction occurs, i.e. until there is no rise in temperature between PSR inlet and exit. The residence time at extinction is the minimum residence time possible for this set of inlet properties. Note that the inverse of residence time is equal to the volume throughput per unit volume of the reactor, i.e.

$$\frac{\dot{V}}{V} = \frac{1}{\tau}$$

where \dot{V} is the volumetric flowrate of gases at exit conditions, V is the volume of the PSR, and τ is the residence time of the PSR. Comparisons of minimum residence times, or maximum volumetric throughputs can be made for different fuel/oxygen/diluent mixtures. A more informative comparison is obtained by taking into account the heating value of the stream passing through the reactor. The heating

value throughput per unit volume of the reactor, $\frac{\dot{Q}_{HV}}{V}$, is related to the residence time, τ , by the following equation:

$$\frac{\dot{Q}_{HV}}{V} = \frac{\rho y_F q_C}{\tau}$$

where ρ is the density in the reactor, y_F is the mass fraction fuel in the reactant stream, and q_C is the heating value of the fuel.

Approach: Choice of Operating Conditions

Combustor conditions were based on the cycle shown in Figure 1. Oxygen from an air separation unit (state 1) mixes with recycled CO_2 (state 7) and enters an isentropic compressor. Fuel from a coal gasification plant or other source (state 2) enters a separate isentropic compressor. The two compressors lead to the inlet of the combustor (states 3 and 4 before mixing). Post-compression temperatures are obtained from STANJAN (Reynolds 1987), using JANAF thermochemical data. Combustion is stoichiometric and occurs at constant pressure. The combustor exit temperature is the same for all cases, because maximum efficiency dictates that the combustor operate at the temperature limited by turbine materials. The combustion products leaving the combustor pass through an isentropic turbine. Then they enter a constant-pressure heat exchanger, heat from which would probably be used in part as input to a Rankine cycle. Water is removed from the combustion products, leaving pure CO_2 (state 7). This CO_2 stream is split into a portion that is recycled into the compressor and a generally much smaller flow that is sequestered.

Temperatures and pressures have the values listed in Table 1 below. The combustor pressure and exit temperature are based on the state-of-the-art GE H series gas turbine combined cycle power plant (Matta et al., 2000). The decisions to treat various devices as isentropic and constant pressure were made for simplicity, and are not expected to affect the relative extinction throughputs for different fuels and degrees of recycle.

Table 1: Power Plant Operating Conditions

Combustor pressure	$P_3=P_4=P_5=23 \text{ atm}$
Combustor exit temperature far from extinction conditions	$T_5=1800 \text{ K}$
O_2 and fuel temperatures at compressor inlets (before mixing with CO_2)	$T_1=T_2=300 \text{ K}$
O_2 and fuel pressures at compressor inlets	$P_1=P_2=1 \text{ atm}$
Turbine exit pressure	$P_6=1 \text{ atm}$
Recycled CO_2 pressure	$P_7=1 \text{ atm}$
Recycled CO_2 temperature	T_7 : variable
Equivalence Ratio	$\phi=1$, except for CH_4/air case, where $\phi=0.5$

With the above specifications, for a given fuel there is one parameter that can be chosen arbitrarily: either the temperature of the recycled CO_2 (T_7) or the degree of dilution of fresh O_2 /fuel mixture with recycled CO_2 . Once one of these has been selected arbitrarily, the other must be chosen to ensure that the adiabatic flame temperature has the specified value. Thus, for relatively high CO_2 recycle temperatures, relatively high dilution levels are required. Required dilution levels were found by trial and error using JANAF thermochemical data and STANJAN (Reynolds, 1987).

Three sets of calculations were performed, corresponding to three types of fuel: pure CH_4 , separated coal gases, and CO/H_2 mixtures. (1) A CH_4/air case served as a baseline to which oxycombustion extinction conditions were compared. This baseline was non-stoichiometric and had no recycled CO_2 . In this case only, the equivalence ratio was chosen to achieve the required post-combustion temperature; the required value of ϕ was 0.5. (2) Four separated coal gas compositions were considered, and are listed in Table 2. These compositions correspond to typical conditions for two different gasification processes (Shell and Texaco), with two different separation processes (polymer and metallic membranes), as reported by Hendriks (1994). They are intended to represent coal gases from which H_2 has been removed for other uses. For each coal gas case, a range of CO_2 recycle temperatures between about 300 and 700 K was considered. The corresponding range of required dilution level is shown in Figure 2, indicating the tradeoff between recycle temperature and dilution level. (3) For a more systematic consideration of the effect of H_2 in the fuel, a series of calculations was performed with different CO/H_2 mixtures as fuel. In these cases, the CO_2 recycle temperature was fixed at 400 K. H_2 mole fraction in the fuel varied between 1% and 50%.

Table 2. Separated coal gas compositions, composition in molar percents (Hendriks, 1994) and heating value, in MJ/ kg fuel

	Texaco/polymer	Texaco/metallic	Shell/polymer	Shell/metallic
CO	73.3	78.0	74.1	87.3
H ₂	18.0	5.0	19.0	4.2
CO ₂	7.0	15.0	0.9	2.0
CH ₄	0.2	0.3	0.0	0.0
N ₂	0.9	1.0	4.7	5.0
Ar	0.6	0.7	1.3	1.5
Heating value, MJ/kg of fuel mixture	11.0	8.7	11.6	9.2

Results and Discussion

Effect of dilution level

Extinction results for the four separated coal gases are shown in Figures 3 and 4. Figure 3 shows the volume throughput per unit combustor volume, at extinction, as a function of recycled CO₂ temperature. In all cases, volume throughput at extinction increases as CO₂ temperature increases, i.e. as dilution level increases, suggesting the desirability of operating with high levels of relatively high-temperature recycled CO₂. When the heating value of the reactant mixture is taken into account, the trend is the same. Figure 4 shows the heating value throughput per volume at extinction for the four fuels. Thus from a combustor throughput standpoint, high levels of dilution with relatively hot CO₂ are best.

The coupled choice of CO₂ recycle temperature and dilution level impacts performance and system costs through many components, not just through the combustor. Other system considerations favor the lowest possible dilution level for two main reasons. First, as the dilution level increases, the heating value per unit volume of reactants decreases, and thus the size of the compressor, turbine, and other hardware must increase for a given power output. Thus capital costs per power output are greater at higher dilution levels. Second, as CO₂ becomes a larger and larger fraction of gas stream passing through compressor and turbine, the thermodynamic efficiency for a given pressure ratio decreases. This decrease occurs because the ratio of specific heats for CO₂ is lower than that of the other mixture components. Although the present study indicates some advantages for the combustor in operating at high dilution levels, it is likely that the best system performance will be achieved with as low a recycle temperature as is practical.

Effect of fuel composition: coal gases and CO/H₂

Figures 3 and 4 also show the effect of fuel composition on extinction conditions. The two coal gases separated with polymer membrane show substantially higher values of both throughput and heating value throughput, compared to the two coal gases separated with metallic membranes. The four fuels have different proportions of H₂, CO, and CH₄, as well as different levels of largely inert compounds: N₂, CO₂, and Ar. Because additional CO₂ dilution levels are chosen to match the adiabatic flame temperature in all cases, the levels of inerts in the fuels are unimportant. As CH₄ levels are never higher than 0.3% of the fuel, the different performance of the different fuels is probably due to the proportions of H₂ and CO present. The higher-H₂ polymer-separated fuels have more vigorous combustion, as indicated by higher heating value throughputs at extinction, than the lower-H₂ metallic-separated fuels, even though combustion occurs at the same temperature.

This effect was investigated more systematically by studying the extinction of CO/H₂ mixtures. In each case, the same precompression CO₂ temperature (T₇=400 K) was used. As always, CO₂ dilution level was chosen so that the adiabatic flame temperature is 1800 K; the required dilution level is shown in Figure 6. Figure 5 shows the heating value throughput at extinction, as a function of the hydrogen content of the

fuel. Consistent with the coal gas results, heating value throughput increases dramatically as H_2 content increases. The relationship is roughly linear. The y-intercept is approximately zero, consistent with the very slow reaction kinetics of CO combustion.

Comparisons to baseline

To evaluate how easy it should be to design a combustor for carbon-sequestering applications, it is useful to compare extinction conditions to those occurring in conventional lean methane-air combustion. With all reactants taken to be at 300 K, an equivalence ratio, ϕ , of 0.5 gives an adiabatic flame temperature of 1800 K. At extinction, the volume throughput and heating value throughput are, respectively, 6330 s^{-1} and 3.95E4 MJ/m^3 . The latter quantity is in the range spanned by the coal gases; it is also equivalent to a mixture of H_2 and CO containing 6.5 % H_2 . Volume throughputs at extinction are high -- roughly ten times as high as the 6.5 % H_2 case, and in fact higher than any of the oxycombustion cases considered.

This disparity in comparisons of volumetric and heat release throughputs at extinction suggests some challenges in adapting combustor design for carbon sequestration. It is interesting to compare lean CH_4 /air to the equivalent (6.5% H_2 in fuel) H_2 /CO/ O_2 /CO₂ mixture. If the H_2 /CO/ O_2 /CO₂ mixture were burned in an existing CH_4 /air combustor, the PSR model predicts the same heating value throughput at the extinction condition. But, because of the differences in extinction throughput, the velocities in the combustor would be a factor of ten lower than for the CH_4 /air case. These low velocities would make the mixing much less vigorous, and thus make the PSR model much less realistic. Clearly combustors would need to be redesigned for oxycombustion, even when used with fuels that are equivalent in terms of maximum heating value throughput. Singh et al. also concluded that combustor redesign would be required when they examined combustion of CH_4 in O_2 /CO₂ (Singh et al. 1999).

Comparing to the baseline lean methane/air case is useful when considering how much H_2 should be removed from a gasification stream. For CO/ H_2 mixtures with very low H_2 mole fractions, required combustor volumes for a given heating value throughput become unwieldy. For example, oxycombustion of a 3% H_2 / 97% CO mixture would require over twice the volume of the CH_4 /air baseline, while the 1% H_2 / 99% CO mixture would require over five times the volume. Thus it appears that H_2 removal may be restricted by the viability of oxycombustors, even if separation technologies improve to allow more effective separation of hydrogen from carbon-rich fuel components.

Conclusions

Perfectly-stirred reactor extinction calculations have been performed for conditions simulating carbon-sequestering oxycombustion of separated coal gases. Recycled CO₂ temperature can be varied along with the degree of dilution with CO₂ in such a way that the mixture's adiabatic flame temperature is held constant. Under those conditions, heat release throughput increases as CO₂ recycle temperature rises between 300 and 750 K. However, other system considerations suggest that the CO₂ recycle temperature should be chosen to be as low as practical. Extinction conditions depend strongly on fuel composition, with much higher heating value throughputs for fuels containing more H_2 . A comparison to CH_4 /air extinction conditions suggests a lower limit on the H_2 content of separated coal gases for practical combustion. Oxycombustion's substantially lower total volumetric flowrates per fuel heating value imply that combustor design will be quite different from existing lean CH_4 /air combustors. Oxycombustor design is also likely to be much less driven by air pollution concerns, allowing more freedom to the designer.

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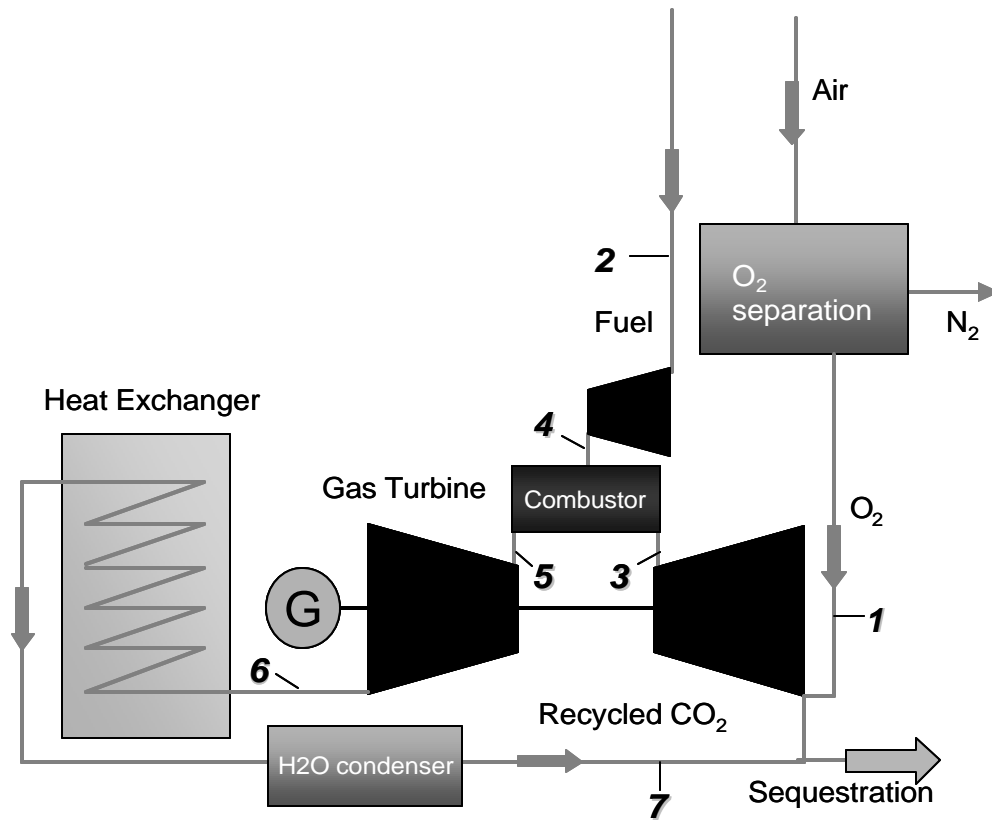


Fig. 1 Schematic of oxycombustion power plant.

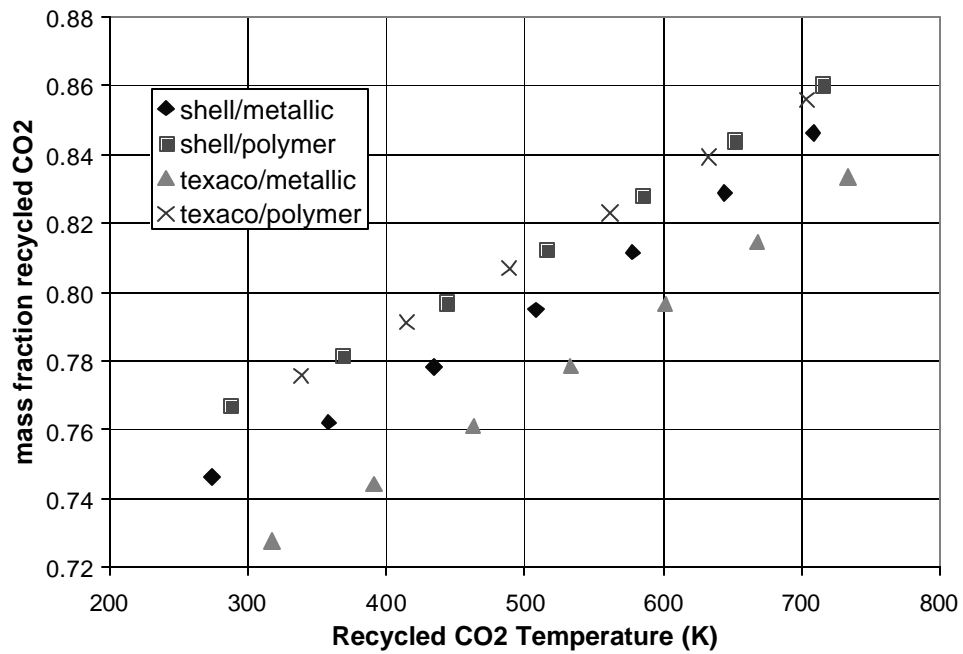


Fig. 2. CO₂ dilution level required to achieve adiabatic flame temperature of 1800 K for stoichiometric oxycombustion of four separated coal gases, as a function of recycled CO₂ temperature.

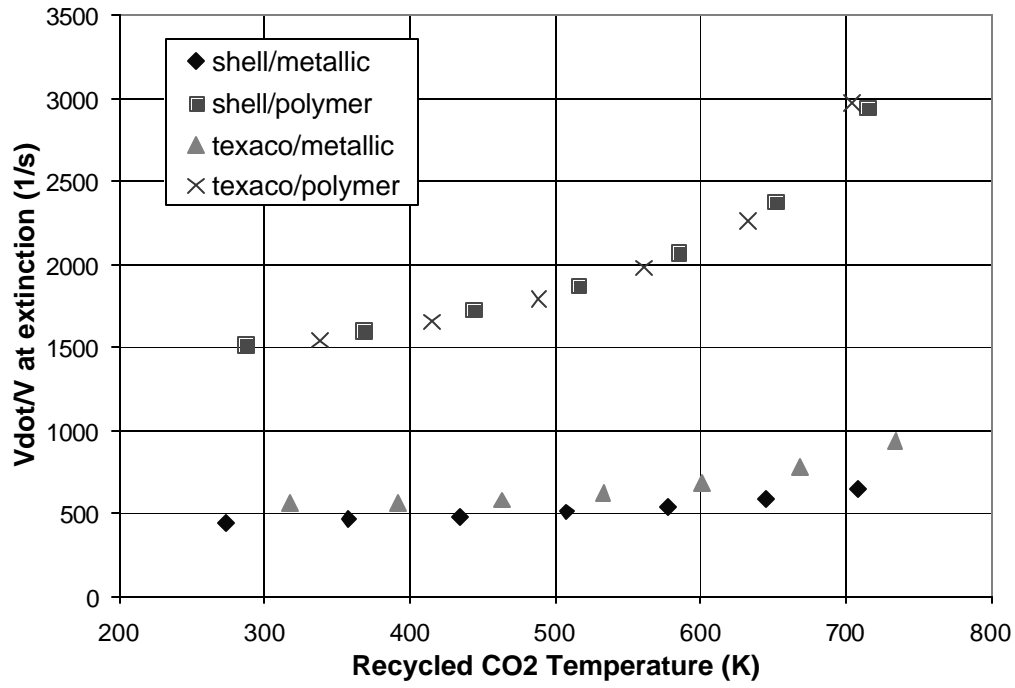


Fig. 3. Effect of recycled CO₂ temperature on volume throughput per unit oxycombustor volume ($\frac{\dot{V}}{V}$) at extinction for four separated coal gases. Dilution level given in Fig. 2.

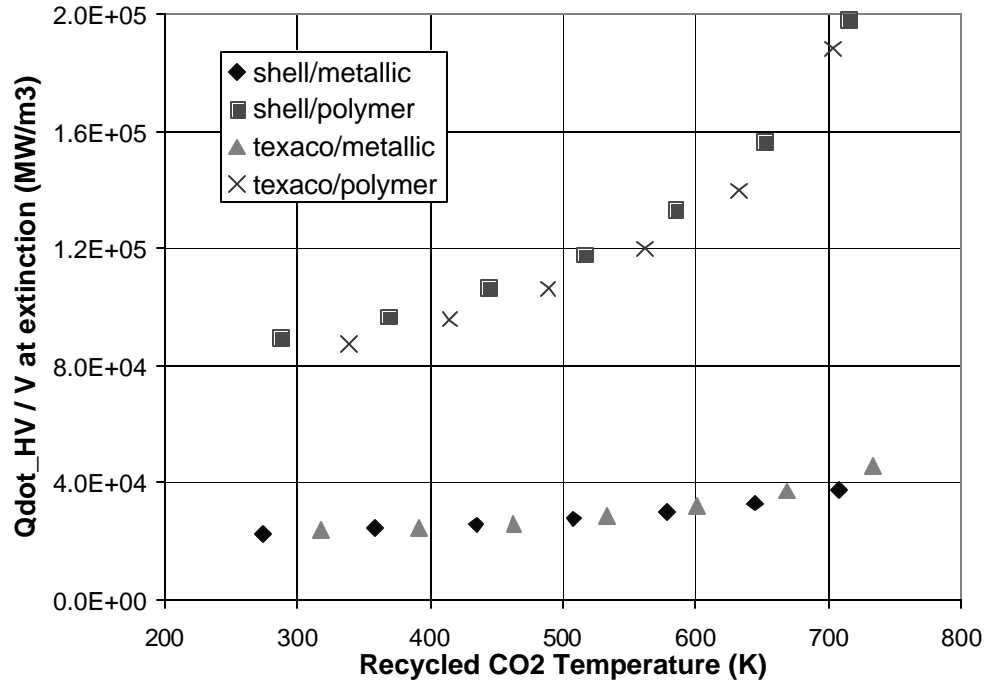


Fig. 4. Effect of recycled CO₂ temperature on heating value throughput per unit oxycombustor volume ($\frac{\dot{Q}_{HV}}{V}$) at extinction for four separated coal gases. Dilution level given in Fig. 2.

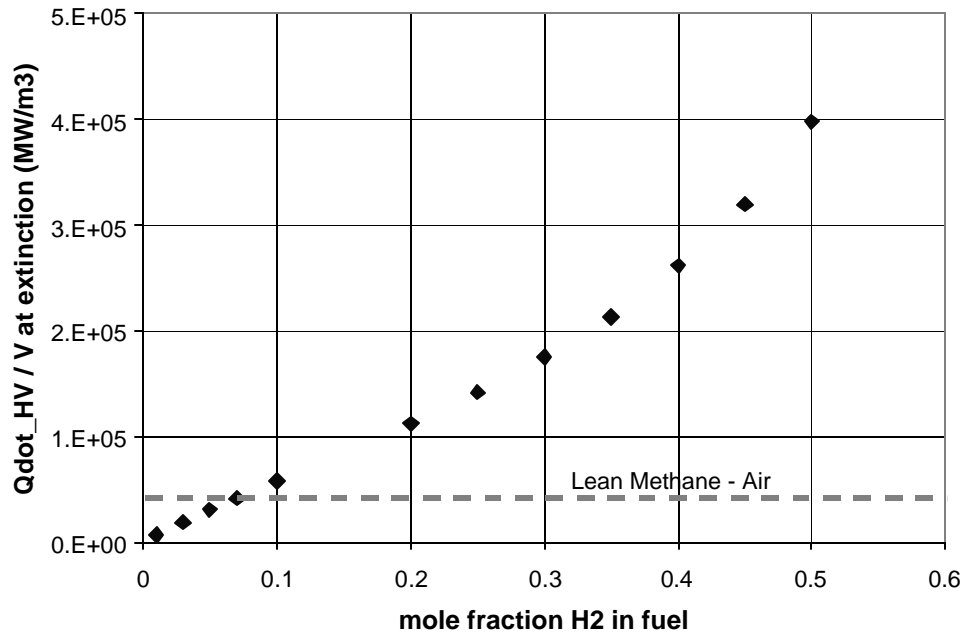


Fig. 5. Effect of fuel composition on heating value throughput per unit oxycombustor volume ($\frac{\dot{Q}_{HV}}{V}$) at extinction for CO/H₂ fuel mixtures. Dilution level given in Fig. 6.

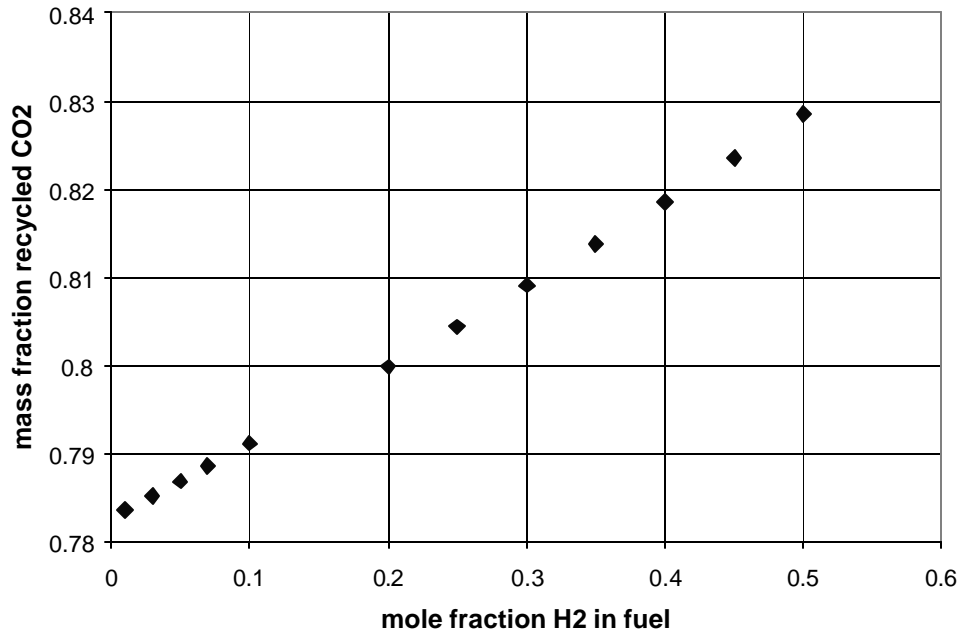


Fig. 6. CO₂ dilution level required to achieve adiabatic flame temperature of 1800 K for stoichiometric oxycombustion of H₂/CO mixtures, as a function of H₂ content of fuel mixture.